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(54) Title: NITROUS OXIDE DECOMPOSITION CATALYST (57) Abstract A method for decomposing nitrous oxide with a catalyst comprising a zeolite which has been at least partially ion-exchanged with at least 1 cation derived from at least one compound selected from the group consisting of hydrogen, ammonium-containing compounds, metals and metal compounds below sodium on the Periodic Table of Elements where the zeolite has a molar ratio of silica to alumina which is controlled to increase catalyst stability. Preferred silica to alumina molar ratios are greater than 55 and more preferably 55 to 200.		

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-1-

NITROUS OXIDE DECOMPOSITION CATALYST

BACKGROUND OF THE INVENTIONFIELD OF THE INVENTION

The present invention relates to a composition and
5 method useful for decomposing nitrous oxide, and more particularly, to a metal promoted zeolite catalyst useful to decompose nitrous oxide.

DESCRIPTION OF THE RELATED ART

Nitrous oxide is coming under increasing environmental
10 scrutiny and has been linked to stratospheric ozone destruction as well as being a suspected contributor to the so-called greenhouse effect. Nitrous oxide is generated in a number of industrial processes. For example, the exhaust gases generated in the manufacture of adipic acid (which is
15 typically commercially produced by oxidation of cyclohexane, cyclohexanol or cyclohexanone in the presence of nitric acid) may contain up to 35 weight percent or more of nitrous oxide. Reference is made to Kroschwitz, et al. editor, Kirk-Othmer, Encyclopedia of Chemical Technology,
20 Fourth Edition, Vol. 1, pp. 466-493, John Wiley and Sons (1991) hereby incorporated by reference for a review of adipic acid including manufacture and processing. The result of the oxidation using nitric acid in the presence of a catalyst includes gaseous waste streams comprising
25 nitric oxides (NO_x) and nitrous oxide (N_2O).

Nitrous oxide can be catalytically decomposed into its constituent elements by contacting the nitrous oxide or nitrous oxide-containing gas with various catalysts such as zeolites, silicas, titania, transition metals and the like.
30 However, such known catalysts typically suffer from one or more deficiencies which make them unsuitable for use in commercial applications. Such deficiencies include thermal and/or mechanical instability; susceptibility to water vapor; nitric oxide/nitrogen dioxide (NO_x) or oxygen

-2-

poisoning or deactivation, particularly at pressures in excess of one atmosphere; too high a light-off or ignition temperature; poor selectivity; and poor activity.

US Patent 5,171,553 discloses a process for the catalytic removal of N_2O gases from gas mixtures. The process is described as being substantially unaffected by the presence of oxygen. A N_2O -containing gaseous mixture is contacted with a catalyst comprising a crystalline zeolite which, at least in part, is composed of five-membered rings having a structure type selected from the group consisting of Beta, MOR, MFI, MEL and FER. Disclosed zeolites under the IUPAC designation (MFI) include but are not limited to ZSM-5, silicalite-1, silicalite, Zeta 1, Zeta 3, NU-3, NU-4 and AZ-1. Disclosed zeolites under the MEL designation include ZSM-11 and silicalite-2, and disclosed zeolites under the FER designation include ferrierite. Representative zeolites of the MOR designation are indicated to include Mordenite, Na-D, Ptilolite and Zeolon. The crystalline zeolite has been at least partially ion exchanged with 0.01 to 15 weight percent of metal selected from the group consisting of copper, cobalt, rhodium, iridium, ruthenium and palladium. Useful mordenites are disclosed to have an Si/Al ratio of from 5 to about 12.5. LZM-5 is indicated to have 78.7 weight percent SiO_2 and 12.5 weight percent Al_2O_3 . ZSM-11 is indicated to have a composition of $0.9 \pm 0.3 M_nO : W_nO_3 : 20 \text{ to } 90 YO_2 : ZH_2O$ wherein M is a cation, n is the valence of the cation, W is aluminum or gallium, Y is silicon or germanium and Z is from 6 to 12. Conditions are disclosed which convert N_2O into gaseous nitrogen and oxygen. US Patent 5,171,533 disclosed a 94% conversion of nitrous oxide at 400°C using copper substituted ZSM-5. A cobalt exchanged Beta zeolite catalyst had a 67% conversion at 400°C. Yuejin Li and John N. Armor (coinventors of US Patent 5,171,553), published Catalytic Decomposition of Nitrous Oxide on Metal Exchanged Zeolites, Applied Catalysis B: Environmental, 1, L21-L29 (1992). Li and Armor which discloses the Si/Al molar ratios of a

-3-

cobalt-Beta zeolite, having a Si/Al molar ratio of 12.9 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ would be 25.8).

Cotton and Wilkinson, Advanced Inorganic Chemistry, Fifth Edition, John Wiley & Sons, pp. 283-286 (1988)

5 reviews zeolites. Zeolites such as ZSM-5 and Silicalite are disclosed to be high silica zeolites. It is further disclosed that catalytic adsorption and ion exchange properties are dependent upon the alumina to silica ratio. The alumina content can be increased or decreased.

10 US Patent Nos. 4,961,917 and 5,024,981 disclose a method for reduction of nitrogen oxides with ammonia using promoted zeolite catalysts. Nitrogen oxides are indicated to have the formula NO_x and normally comprise a mixture of NO and NO_2 . A gaseous stream of nitrogen oxides and ammonia,
15 which may also contain oxygen, is contacted at a temperature of from 250-600°C with a sulfur tolerant catalyst composition. The catalyst composition comprises a zeolite having a silica to alumina ratio of at least about 10 and preferably in excess of the minimum of 10. The
20 utilization of high ratios of silica to alumina is disclosed to enhance acid resistance of the zeolite and to provide enhanced resistance of the zeolite to sulfur poisoning. Zeolites resistant to sulfur poisoning include those having a pore diameter of at least 7 Angstroms and
25 are interconnected in three dimensions. Useful zeolites are disclosed to include Y, Beta and ZSM-20. Specifically, it is disclosed that conversion efficiencies of 90-93% for NO_x reduction with ammonia had been obtained with fresh copper promoted zeolites having silica to alumina ratios of 20,
30 26, 28, 37 and 62. A conversion efficiency of 77% was attained by a fresh copper promoted ZSM-5 zeolite having a silica to alumina ratio of 46. For USY, silica to alumina ratios are disclosed to be less than 30.

US Patent No. 4,507,271 is directed to the removal of
35 nitrous oxide from gases containing hydrogen, nitric oxide and nitrous oxide by a process in which the gases are treated with molecular sieves. Preferred molecular sieves

-4-

are A-, X- or Y- zeolites as well as natural zeolites such as mordenite, faujasite or chabazite. The molecular sieves used are indicated to pore sizes from 4 to 10 and in particular 5 to 9 Angstroms. It is reported that prior to
5 treatment, it is desirable to remove water from the nitrous oxide containing gas.

US Patent No. 4,259,303 is directed to a system for treating waste anesthetic gas by contacting the laughing gas contained in the waste anesthetic gas with a catalyst
10 comprising one or more metal oxides selected from the group consisting of ferric oxide, cobalt oxide, cupric oxide, chromium oxide, manganese dioxide and nickel oxide. It is disclosed that any of the metal oxides may be used in granular, spherical or powdered form, or may be supported
15 on a carrier to increase the surface area of the catalyst. Examples of carriers used include alumina, silica and titania. German Preliminary Publication Application OS DE 3,543,640/87A1 discloses the catalytic decomposition of nitrous oxide. The catalyst uses palladium. The
20 palladium can be carried on a variety of inert carrier materials including aluminum oxide, corundum, alumina, porcelain, silicas, natural or synthetic silicates, quartz, titanium dioxide or lithium-aluminum spinel.

US Patent No. 5,200,162 discloses a process for the
25 decomposition of nitrous oxide to nitrogen and oxide. Useful catalyst are disclosed to include metal oxides, metals, zeolites, and a variety of other materials.

A variety of journals have addressed the use of transition metal exchange zeolites as catalysts for redox
30 reactions including the reduction of nitrous oxide. Such articles include Winter, The Decomposition of N₂O on Oxide Catalysts, Journal of Catalysis 34, 431-439 (1974); Aparicio and Dumesic, Kinetic Modeling Studies of Transition Metal-Exchanged Zeolites as Catalysts for Redox
35 Reactions, Journal of Molecular Catalysis, 49 (1989) 205-221; Fu, et al., Decomposition of Nitrous Oxide on FeY Zeolite, Journal of Catalysis 68, 166-171 (1981); Panov, et

-5-

al., The Role of Iron in N₂O Decomposition on ZSM-5 Zeolite and Reactivity of the Surface Oxygen Formed, Journal of Molecular Catalysis 61 (1990) 85-97; Dumesic and Millman, Redox Catalysis in Zeolites, 1990 American Chemical Society, 0097-6156/90/0437-0066\$06.00/0.

Other disclosures relating to the control of nitrous oxide of interest include: Muzio, et al., N₂O Formation in Selective Non-Catalytic NO_x Reduction Processes; and Peters, et al., A Solid Chemical Air Generator, Amoco Chemicals Corporation, AMRL-TDR-64-71, September, 1964.

US Reissue Patent 28,341 of US Patent 3,308,069 is directed to Beta Zeolites. The silica to alumina ratio for Beta zeolite is disclosed to range from about 10 to about 200. Additionally, Beta zeolites are described in references such as Bonetto, et al., Optimization of Zeolite-Beta in Cracking Catalysts, Influence of Crystallite Size, Applied Catalysis, pp. 37-51 (1992) which describes Beta zeolite as being a 12-member ring tridirectional zeolite with two types of channels, one being about 7.0 and the other about 5.5 angstroms. Beta zeolites can be synthesized within a large range of silica to alumina ratio, (12 to 200). Further it is disclosed that Beta zeolite could be useful as a catalyst, since it combines characteristics of large pore size, high silica to alumina synthesis ratio and tridirectional network of pores. The structural characteristics of Beta zeolites are also reviewed in Newsam, et al., Structural Characterization of Zeolite Beta, Proc. R. Soc. Lond. A 420.375-405 (1988).

Nitrous oxide is receiving more importance due to its link to destruction of the ozone layer. Accordingly, it is a continuing goal to reduce the amount of nitrogen oxides in commercial effluent streams vented to the atmosphere. Commercially, long-term catalytic stability becomes an important criteria in selecting a catalyst composition.

-6-

SUMMARY OF THE INVENTION

The present invention relates to a method of catalytically reducing nitrous oxide with a catalyst comprising zeolite. Zeolite catalyst stability has been
5 found to be related to the molar ratio of the silica to alumina of the zeolite.

The effectiveness of a catalyst in reducing nitrous oxide to nitrogen and oxygen is indicated by the temperature (T_{50}) at which 50 percent (typically measured
10 based on parts per million by volume) of the nitrous oxide is converted to nitrogen and oxygen. This is also referred to as the "light off" temperature. The light off temperature is preferably as low as possible while obtaining a satisfactory reduction of nitrous oxide. If the
15 light off temperatures are too high, then the reduction reaction is ineffective. Satisfactory catalyst performance is typically obtained at light off temperatures up to 450°C and more preferably up to 425°C.

As the catalyst ages under reaction conditions, the
20 light off temperature has been generally found to increase making the catalyst less effective at low temperatures. It is desirable to maintain the light off temperatures below 450°C and more preferably below 440°C, yet more preferably below 430°C upon aging in air for 8,000 hours at 775°C. This
25 is accomplished by the method of determining the silica to alumina ratio of a particular zeolite based catalyst at which the stability of the zeolite is maintained to result in a light off temperature of less than 450°C after the zeolite has been aged in air for 8,000 hours. The most
30 preferred zeolite catalyst is a Beta zeolite which has been at least partially ion-exchanged with a transition metal, most preferably cobalt. In accordance with the method of the present invention, this catalyst is controlled to have a silica to alumina ratio sufficient to have a light off
35 temperature after 8,000 hours of aging in air at 775°C of less than 440°C and preferably less than 430°C. The preferred method of controlling the silica to alumina ratio

-7-

is to increase the molar ratio of silica to alumina by dealuminating the catalyst.

A preferred method of the present invention comprises reducing nitrous oxide, preferably nitrous oxide which is
5 part of a gaseous stream. The method comprises controlling, typically by increasing, the molar ratio of silica to alumina of a catalyst comprising a zeolite, which has been partially ion exchanged with at least one cation derived from at least one compound selected from the group
10 consisting of metals and metal compounds wherein the metal is selected from the group of metals below sodium on the Periodic Table of Elements, ammonium and hydrogen. The molar ratio of silica to alumina is increased sufficiently to increase the catalyst stability. The catalyst with the
15 increased silica to alumina ratio is contacted with a gaseous stream under conditions sufficient to reduce at least part of the nitrous oxide to nitrogen and oxygen. The zeolite preferably has a molar ratio of silica to alumina of at least 55, preferably from about 75 to about
20 200, more preferably from about 80 to about 175 and most preferably from about 80 to about 120.

Preferred zeolites are crystalline zeolites having a pore size of at least 4.0 Angstroms with a more preferred pore size of from 6 to 8 Angstroms. More preferred zeolites
25 are selected from the group consisting of Beta, ZSM-5, Y, mordenite and chabazites, with the more preferred zeolites being Beta and ZSM-5, and the Beta zeolites being most preferred.

The compound with which the zeolite is partially ion
30 exchanged can be a hydrogen, an ammonium compound, a metal or metal compound wherein the metal is selected from the group consisting of metals Periodic Table Groups 1A, 2A, 3A, 1B, 2B and transition metals having atomic numbers from Periodic Table Groups 21 to 28, 39 to 46 and 72 to 78.
35 Particularly preferred metals are selected from the group consisting of cobalt, copper, rhodium, iridium, ruthenium and palladium. The most preferred metal is cobalt. The

-8-

zeolite is preferably exchanged with at least 0.01, preferably from 0.01 to about 15, more preferably from 0.5 to 8, and most preferably 2 to 5 weight percent of the metal based on the total weight of the catalyst. Useful
5 metal compounds include metal oxides and metal salts.

The nitrous oxide is reduced at temperatures of from about 200°C to about 800°C and pressures from about 0.1 to about 300 atmospheres. Preferred gas stream velocities through a fixed bed reactor are gas streams having an
10 hourly space velocity of from 1,000 to 300,000 and more preferably from 5,000 to 30,000 hours⁻¹.

As minor amounts of nitrous oxide in waste gases are being defined as more environmentally significant, the effectiveness of catalysts for reducing nitrous oxide in
15 waste gas to nitrogen and oxygen over long periods of time is necessary for economical treating such gas streams. The improvement of the present invention relates to increased catalyst stability with respect to conversion of nitrous oxide at low temperatures by controlling the silica to
20 alumina ratio. In particular, for preferred zeolites such as Beta zeolites, it has been found that improved long term stability with regard to reducing nitrous oxides to nitrogen and oxygen can be effectively achieved by using such zeolites having silica to alumina molar ratio of from
25 55 to about 200. This improvement in stability has made the use of such zeolitic catalyst commercial viable.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph of the conversion temperature (T_{50}) at which 50% of nitrous oxide in a gas stream consisting of
30 17 molar percent nitrous oxide, 2% oxygen, about 2% H₂O, about 400 part per million (ppm) NO, was passed through a three inch catalyst bed at 20 psig and a space velocity of 20,000 reciprocal hours VHSV versus hours of aging in a static muffle oven in air at 775°C.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

-9-

The present invention relates to a method of reducing nitrous oxide to nitrogen and oxygen. In accordance with the present method, nitrous oxide can be catalytically reduced in the presence of water, oxygen and/or nitrogen oxides (NO_x). The catalyst of the present invention has been found to be thermally stable. The process is directed to contacting the gaseous stream with a zeolite catalyst. The zeolite catalyst has a silica to alumina molar ratio which results in improved catalyst stability with regard to its ability to convert the nitrous oxide to nitrogen and oxygen at low light off temperatures over extended periods of time.

For the purposes of the present invention, catalyst stability is indicated by the light off temperature (T_{so}) at which there is conversion of 50 percent of the nitrous oxide to nitrogen and oxygen after aging the catalyst in air at 775°C for 4,000, and more preferably for 8,000, hours. Preferably the T_{so} for nitrous oxide reduced using the catalyst of the present invention upon such aging is less than about 450°C and more preferably less than 430°C after air aging at 775°C for 4,000 hours and preferably 8,000 hours or more.

To illustrate the improvement of the present invention, the stability is measured by measuring the decomposition of nitrous oxide in a one-inch diameter upflow reactor. A gas feed consisting of 17 mole percent N_2O , 2 mole percent O_2 , 2 mole% H_2 , 400 ppm NO , and the balance being N_2 is passed through a three-inch bed of catalyst extrudate at 20 psig and 20,000 reciprocal hours (volume per hour per standard volume (VHSV)). The reactor is then heated at a rate of 10°C per minute. Thermocouples are located 0.5 inches before and after the catalyst bed to measure the reaction temperature. During heat up, gas samples are continuously taken before and after the catalyst bed and sent to an on-line Beckman oxygen analyzer, Model OM-11EA. The nitrogen decomposition reaction ($\text{N}_2\text{O} \rightarrow \text{N}_2 + 0.5 \text{O}_2$), is monitored as a function of

-10-

increased outlet O_2 concentration versus inlet bed temperature. Catalyst activities are expressed in terms of the inlet bed temperature (T_{so}), referred to as the light off temperature, at which 50% of the N_2O had decomposed. The lower the resulting light off temperature the more active the catalyst. Stability is determined by aging the catalyst in a static muffle oven in air at 775°C. Catalyst samples are removed periodically for activity evaluation.

The method of the present invention involves the reduction of nitrous oxide with catalyst comprising zeolite having a molar ratio of silicon to alumina of at least 55, which has been at least partially ion exchanged with at least one compound selected from the group consisting of metals below sodium on the periodic table of elements, ammonium and hydrogen. Preferred zeolites have a pore size of at least about 4, and preferably 6 to 8, angstroms. Particularly preferred zeolites are selected from the group consisting of Y, Beta, ZSM-5, mordenite and chabazite, with Beta and ZSM-5 more preferred and Beta most preferred.

Reference is made to a description of useful zeolites for the process of the present invention in Ocelli and in Breck, Zeolite Molecular Sieves, Structure, Chemistry, and Use, John Wiley & Sons (1974), hereby incorporated by reference. Reference is made to Breck for a description of Beta zeolite. US Patent 3,308,069 reissued as Reissue Patent 28,341 also discloses Beta zeolites and their methods of manufacture and are hereby incorporated by reference. References reviewing Beta zeolites are listed in the above description of related art including the Bonetto and Newsam articles both hereby incorporated by reference. Beta zeolite is disclosed to have silica to alumina molar ratios of from 10 to 200.

ZSM-5 is commercially available and can be prepared by procedures disclosed in US Patent 3,702,886, hereby incorporated by reference. Mordenite is referred to in US Patent 5,171,553, hereby incorporated by reference, and includes synthetic and naturally occurring zeolites having

-11-

the mordenite topology as included under the general IUPAC Structural Code of Mordenite (MOR). Zeolite Y is reviewed in Occelli and Robson, Molecular Sieves, Synthesis of Microporous Materials, Vol. 1, Chapter 3, pp. 31-41, 5 VanNostrand Rheinhold, New York, 1992. Chabazite is also referred to in Occelli at Chapter 9, pp. 105-108.

The zeolite preferably has a molar ratio of silica to alumina of at least 55, preferably from about 75 to about 200, more preferably from about 80 to about 175 and most 10 preferably from about 80 to about 120. The molar ratio of silica to alumina of the zeolites used to prepare the catalyst compositions is typically increased to a level above the ratio normally obtained when the zeolites are commercially produced. Thus, when Beta zeolite is prepared 15 by the method, such as disclosed in US Patent 3,308,069, it will typically have a molar ratio of silica to alumina of about 35 when measured by chemical analytic methods. This is notwithstanding the broad disclosure of beta zeolite having a silica to alumina ratio of 10 to 200.

20 The silica to alumina molar ratio may be increased, for example, by reacting the Beta zeolite with an acid. Scherzer, The Preparation and Characterization of Aluminum-Deficit Zeolites, Catalytic Materials, American Chemical Society 1984 (0097 6156/84/0248 0157), pp. 157-200, is 25 directed to methods of preparation of aluminum-deficient zeolites. Three methods include thermal or hydrothermal dealumination; chemical dealumination; and a combination of thermal and chemical dealumination. While thermal or hydrothermal treatment can be used, this results in a 30 partial framework dealumination with the aluminum remaining in the zeolite cages or channels. The preferred chemical treatment can be carried out with a variety of reagents and results in the removal of aluminum from the zeolite in a soluble or volatile form. The preferred chemical 35 dealumination can be achieved by reacting the zeolite with a suitable reagent in solution (aqueous or nonaqueous); or by reacting the zeolite with a reagent in the vapor phase

-12-

at high temperature. Preferably dealumination is accomplished in solution by reacting the zeolite with solutions of acids, salts or kelating agents and most preferably acids. Useful acids include mineral acids such as sulfuric acid, hydrochloric acid and nitric acid with sulfuric acid most preferred. Breck, supra, discloses that aluminum may be removed from the framework of certain zeolites by the treatment with acids and gives examples of increasing the silicon to alumina ratio by treatment with hydrochloric acid (Breck, supra, pp. 505-507).

The zeolite and the acid are preferably reacted at ambient temperature and pressure in a reaction vessel. The resulting reaction product is separated and washed with deionized water and filtered. The reaction product is then dried. The molar ratio of silica to alumina can be determined by known methods, preferably X-ray fluorescence. A preferred analytic procedure for determining the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is to calcine a sample for one hour at $1,000^\circ\text{C}$. The sample is mixed with ten parts by weight of a fluxing agent, preferably an 80/20 weight ratio of lithium metaborate to lithium tetraborate. The mixture is fused for about 5 minutes at $1,200^\circ\text{C}$. The resulting mixture in the form of a button is analyzed by X-ray fluorescence. This is done using a reference comparison.

The zeolites useful in the present invention are preferably promoted by a metal, preferably by ion exchange. Preferably the metal is provided by a metal or metal compound, with the metal being selected from the Periodic Table Groups consisting of 1A, 2A, 3A, 1B, 2B and transition metals having atomic numbers from 21 to 28, 39 to 46 and 72 to 78. Particularly preferred metals are selected from the group consisting of cobalt, copper, rhodium, iridium, ruthenium and palladium with cobalt being most preferred in the catalyst of the present invention. Preferably the zeolite is ion exchanged with from 0.01 to about 15, preferably 0.5 to 8 and more preferably 2 to 5 weight percent of the metal based on the total weight of

-13-

catalyst. The metal can be provided as a pure metal or metal containing compound such as metal oxides or salts.

The catalyst compositions of the present invention can be prepared by standard methods known to those skilled in the art. The zeolites can undergo certain exchange reactions as disclosed in Breck, supra. For example, a cobalt promoted Beta zeolite catalyst composition can be prepared by contacting a calcined Beta zeolite powder (prepared by the method of US Patent 3,308,069) with a solution of a soluble cobalt salt such as cobalt nitrate or cobalt sulfate. The contacting is preferably performed at a pH of about 7.5 for a period of about 1 hour and at an elevated temperature preferably about 75°C to about 85°C. The time and temperature may be varied and are not considered critical to the preparation of the catalyst compositions of the invention. The metal promoted zeolite is then collected and purified by standard procedures, for example, filtration and water washing. The collected zeolite may then be dried, e.g., at 100°C and may be extruded into a desired shape by first mixing with known excipients such as a polymethylated cellulose ether and colloidal silica in the presence of water to produce an extrudible putty. In a preferred method a solution of the metal compounds, i.e., cobalt compound, can be impregnated into a zeolite powder by an incipient wetness method. The solution is mixed into the dry powder. The composition, which appears as a powder, is then dried at a suitable temperature, preferably 75°C to 125°C. The resulting zeolite is impregnated with the cobalt compound at least part of which is believed to undergo ion exchange with the cation of the zeolite.

The amount of metal which has undergone an exchange reaction and is incorporated into the zeolite can be determined by atomic adsorption by means known in the art. Preferably, a sample is dissolved in a 3:1 weight ratio of hydrofluoric acid and perchloric acid and then dried. The resulting powder is then redissolved in a 50% aqueous

-14-

hydrochloric acid solution and analyzed by atomic adsorption using a reference comparison.

The Beta zeolites are preferably made using an organic template such as tetraethyl ammonium hydroxide (TEAOX). The
5 organic compound is removed (destroyed) during thermal treatment without damaging the zeolite structure. This can be accomplished by gradually increasing the temperature, typically in step increases.

The zeolite catalyst can be provided in a fine powder
10 form which is admixed with a suitable refractory binder such as bentonite or silica and formed into a paste which can be extruded or formed into a slurry which can be coated onto a suitable substrate such as a honeycomb carrier. Honeycomb carriers comprise one or more refractory bodies
15 having a plurality of fine, parallel gas flow passages extending therethrough. Such carriers are well known in the art and may be made of any suitable material such as cordierite or the like. Zeolite catalysts of the present invention can also be provided in the form of extrudates,
20 pellets, tablets or particles of any suitable shape, for use as a packed bed or particulate catalyst, or as shaped pieces such as plates, saddles, stars, tubes or the like.

The catalysts of this invention can optionally be subjected to thermal treatment prior to use. The thermal
25 treatment may be conducted in the reactor prior to contacting the reactants with the catalyst or as a separate step. The thermal treatment comprises heating the catalysts of this invention to above ambient temperature, preferably between 80°C and 150°C while under an inert atmosphere of
30 about 1 to 220 atmospheres for a period ranging from about 0.5 to 12 hours to remove residual moisture. The catalyst may be dried during one or more periods utilizing one or more discrete temperatures or temperature ramping techniques known in the art. The dehydration can be carried
35 out by any method capable of removing water from the catalyst without causing structural collapse of the zeolite structure.

-15-

In accordance with the process of the present invention, a gas stream comprising nitrous oxide is contacted with the catalyst of the present invention. The gas can pass through a bed of the catalyst composition of the invention housed in a suitable container at a flow rate and at a temperature sufficient for the decomposition of the nitrous oxide into its elemental components nitrogen and oxygen. Alternatively, the catalyst can be applied to a substrate such as a honeycomb and the gas stream passed through the honeycomb to contact the catalyst.

The amount of catalyst to be utilized in the present process varies depending upon the reaction conditions (i.e., temperature, pressure and the like), and the amount of N_2O residing in the process stream to be treated. Desirably, an effective amount of catalyst is used, i.e., the amount which causes a reaction to occur when N_2O is placed in contact with the enumerated catalysts under the specified reaction conditions. The catalysts of the invention can be fabricated onto fire-proof supports known in the art. A preferred support has a honeycomb design whereby surface area is maximized to enhance catalytic activity.

The process according to this invention is typically run at temperatures ranging from about $200^{\circ}C$ to $800^{\circ}C$ and pressures between about 0.1 and 300 atmospheres. However, higher temperatures may be utilized because the maximum temperature for conducting the process is limited only by the temperature stability of the zeolite itself. More particularly, the process can be advantageously run under fixed bed conditions at temperatures ranging from about $250^{\circ}C$ to $800^{\circ}C$ and a gas hourly space velocity ranging from 1,000 to 300,000 hr^{-1} , preferably 5,000 hr^{-1} to 30,000 hr^{-1} .

Known nitrous oxide decomposition catalysts are unstable or subject to deactivation when water, oxygen and/or NO_x are present in the nitrous oxide containing gas stream. The catalyst compositions of the present invention unexpectedly possess improved stability characteristics

-16-

over prior art catalysts when subjected to these additional gas stream components.

The method of the present invention can be used to improve various industrial processes which result in the formation of gas streams comprising nitrous oxides. Such processes include the production of adipic acid as disclosed in Kroschwitz, et al., Editor Kirk-Othmer, supra. US Patent No. 5,200,162 discloses that a significant source of nitrous oxide is disclosed to be in waste gases from adipic acid manufacture, where nitrous oxide formation accompanies the nitric acid oxidation of cyclohexanone. Muzio, et al., supra, addresses the control of nitrous oxide formation from selective non-catalytic nitric oxide reduction processes. Representative processes selective non-catalytic reduction processes include ammonia injection, urea injection and cyanuric acid/cyanic acid injection. US Patent No. 4,259,303 recognizes waste anesthetic gas streams which contain nitrous oxide. The amounts of nitrous oxide in anesthetic gas streams can be as high as 75 volume percent and are typically as high as from 50 to 75 percent by volume. Nitrous oxide is formed in a process for the preparation of hydroxyl ammonium salts by catalytic hydrogenation of nitric oxide with hydrogen as recited in US Patent No. 4,507,271. Resulting gas streams can contain up to 15 volume percent and typically 3 to 15 volume percent of nitrous oxide. US Patent No. 5,200,162 also discloses that nitrous oxides are formed from a variety of industrial processes. Off gases from nitric acid plants are recognized as a source of nitrous oxide. Other nitrous oxide sources are from the production of hydroxyl amine derivatives, caprolactam production, and the low temperature combustion of nitrogen containing materials such as in fluid bed incinerators. Waste gases are disclosed to be in concentrations as high as 30 volume percent of nitrous oxide.

The various industrial processes disclosed above and otherwise existing resulted in waste gas streams containing

-17-

as much as 75 volume percent of nitrous oxide or more. It is desirable to treat these streams in accordance with the process of the present invention to substantially reduce the nitrous oxides to nitrogen and oxygen. Preferably the processes conducted to reduce the amount of nitrous oxide in the stream to below 100, preferably below 50, and more preferably below 25 parts per million by volume. Most preferably, the process is conducted to substantially eliminate the nitrous oxide in the waste stream. Alternatively, at least 95 and more preferably at least 99 percent of the nitrous oxide in the gas stream is decomposed.

The following examples are provided to further illustrate various embodiments of this invention and to provide a comparison between the enumerated catalysts of this invention and prior art catalysts for destroying N_2O , in N_2O containing gas streams. These examples are provided to illustrate the nature of the process described herein and are not intended to limit the scope of the claimed invention.

Reference is made below to the weights of solids being on a "vf" (volatile-free) basis. This term is used to indicate the weight that the solid in question would have if it were calcined at $1000^\circ C$ for one hour to drive off volatiles. Ratios of SiO_2/Al_2O_3 are molar ratios and percents are weight percents unless stated otherwise.

EXAMPLES

EXAMPLE 1 (Beta Zeolite: $SiO_2/Al_2O_3 = 34.4$)

The following materials were combined in a 100 gallon, titanium lined, autoclave reactor and stirred sufficiently to maintain the solids in suspension:

1. 146.6 lbs. HI-SIL® 233 silica powder made by PPG;
2. 6.0 lbs. Nalco 680-W™ sodium aluminate made by Nalco Chemical Co.;
3. 13.4 lbs. Nyacol Al-20, colloidal alumina made by Nyacol Products, Inc.;

-18-

4. 551.2 lbs. of solution #1 containing 1.09 wt.% SiO_2 , 0.37 wt.% Na_2O , 2.00 wt.% TEAOH (tetraethylammonium hydroxide), and 96.5 wt.% H_2O ; and
5. 105.8 lbs. of solution #2 containing 40.00 wt.% TEAOH and 60.0 wt.% H_2O ; and
6. 7.2 gal deionized water

The reactor was sealed and heated to 305°F with continuous stirring. After 4 days (about 96 hours) at 305°F, the reactor was cooled and the product solids were separated from the reaction liquor using a 12 square-inch filter press in 3 batches. Each filter cake batch was washed with about 30 gallons of deionized water then dried at 100°C. The dried solids were then calcined for 2 hours at 700°F followed by 2 hours at 1100°C. The resulting calcined powder had a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 34.4 (by X-ray fluorescence) and a BET surface area of 697 m^2/g . Analysis by X-ray diffraction showed the characteristic peaks associated with Beta zeolite (per U.S. patent 3,308,069).

20 COMPARATIVE EXAMPLE 2 (2.62%Co/Beta + 15% SiO_2)

125 g of the calcined Beta powder of Example 1 were added (with stirring) to 341 g of an aqueous solution of $\text{Co}(\text{NO}_3)_2$ containing 1.73 wt.% Co. The pH of the slurry was then adjusted to about 7.5 using a 50/50 (by weight) solution of concentrated NH_4OH (14.8 M) and deionized water. With continued stirring, the pH adjusted slurry was heated to 82°C and reacted for 1 hour. The slurry was then vacuum filtered and washed with 1.25 liters of deionized water. The filter cake was dried at 100°C, resulting in a cobalt promoted Beta zeolite powder containing 2.62%(vf) Co (expressed as the metal) and 0.11%(vf) Na_2O .

75 g(vf) of the Co promoted Beta zeolite was then thoroughly mixed with 2.3 g of Methocel 20-121 cellulose ether, 33.4 g Ludox(R) AS-40 colloidal silica and about 70 g of deionized water. The resulting "putty" was extruded by hand using a 60 cc plastic syringe having a 0.063 inch

-19-

aperture. These silica bound extrudates were oven dried at 100°C then calcined for 1 hour at 1000°F.

EXAMPLE 3 (Beta Zeolite: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35.4$)

The following materials were combined in a 5,000 gallon stainless steel autoclave reactor and stirred sufficiently to maintain the solids in suspension:

1. 4,048 lbs. HI-SIL® 233 silica powder made by PPG;
2. 292 lbs. Nalco 680-W™ sodium aluminate made by Nalco Chemical Co.;
- 10 3. 100 lbs. Nyacol Al-20, colloidal alumina made by Nyacol Products, Inc.;
4. 5,593 lbs. of solution #1 containing 0.85 wt.% SiO_2 , 0.25 wt.% Na_2O , 1.60 wt.% TEAOH (tetraethylammonium hydroxide), and 97.0 wt.% H_2O ; and
- 15 5. 6,461 lbs. of solution #2 containing 20.00 wt.% TEAOH, and 80.0 wt.% H_2O ; and
6. 865 gal. deionized water

The reactor was sealed and heated to 305°F with continuous stirring. After 4 days at 305°F, the reactor was cooled and the product solids were separated from the reaction liquor using a filter press. The filter cake was washed with several gallons of deionized water per gallon of reaction mixture, re-slurried at about 20% solids then spray dried. Next, the spray dried solids were calcined for 25 2 hours at 700°F, followed by 2 hours at 1100°F. The resulting calcined powder had a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35.4 (by chemical analysis) and a BET surface area of 590 m^2/g . Analysis by X-ray diffraction showed the characteristic peaks associated with Beta zeolite (per U.S. 30 patent 3,308,069).

EXAMPLE 4 (Beta Zeolite: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 118$)

The following materials were combined in a glass beaker and stirred sufficiently to maintain the solids in suspension:

- 35 1. 412.3 g calcined Beta zeolite powder made in Example 3;

-20-

and

2. 730.5 g 10 wt% H_2SO_4 aqueous solution.

After 16 hrs. of continuous stirring at room temperature, the slurry was vacuum filtered then washed with 2 liters of deionized water. The resulting filter cake was re-slurried to 35% solids with deionized water, vacuum filtered, washed with 2 additional liters of deionized water then dried at 100°C. The resulting Beta zeolite powder had a molar SiO_2/Al_2O_3 ratio of 118 (by X-ray fluorescence), a BET surface area of 620 m^2/g and containing 0.01%(vf) elemental sulfur. Analysis by X-ray diffraction showed the characteristic peaks associated with Beta zeolite (per U.S patent 3,308,069).

EXAMPLE 5 (3.94 wt.%Co/Beta[118] + 15% SiO_2)

An incipient wetness impregnation was carried out as follows: 12.32 g of $Co(NO_3)_2 \cdot (H_2O)_6$ were dissolved in 25 ml of deionized water then added to 50 g(vf) of the Beta powder of Example 4 and then thoroughly blended. The wet powder was dried at 100°C, resulting in a cobalt promoted Beta zeolite product containing 3.94%(vf) Co (expressed as the metal) and 0.04%(vf) Na_2O .

The above Co promoted Beta zeolite[118] was then thoroughly mixed with 5.0 g of Methocel 20-121 cellulose ether, 22.3 g Ludox(R) AS-40 colloidal silica and about 40 g of deionized water. The resulting "putty" was extruded by hand using a 60 cc plastic syringe having a 0.063 inch aperture. These silica bound extrudates were oven dried at 100°C then calcined for 1 hour at 1000°F.

CATALYST EVALUATION PROCEDURE

N_2O decomposition tests were conducted in a 1" diameter upflow reactor. A feed gas consisting of N_2O (17 mole %), O_2 (2.0 mole %), H_2O (~2%), NO (400 ppm) and N_2 (balance) was passed through a given 3 inch bed of catalyst extrudates (Examples #2 and 5) at 20 psig and 20,000 hr^{-1} VHSV (volume of gas per hour divided by volume of catalyst). The

-21-

catalyst was in pellet form with the pellets being about 1.3 mm in diameter and 3.5 mm long. The reactor was then heated at a rate of 10°C/min. Thermocouples were located about 0.5 inches before and after the catalyst bed to measure the reaction temperature. During heat-up, gas samples were continuously taken from before and after the catalyst bed and sent to an on-line Beckman oxygen analyzer (Model OM-11EA). Measurements were made in parts per million by volume.

The N_2O decomposition reaction ($N_2O \rightarrow N_2 + 0.5 O_2$) was monitored as a function of increased outlet O_2 concentration vs. inlet bed temperature. Catalyst activities were then expressed in terms of the inlet bed temperature at which 50% of the N_2O had decomposed. Thus, the lower the resulting temperature the more active the catalyst.

Aging was carried out in a static muffle oven in air at 775°C. Samples were removed periodically for activity evaluation. Results of the catalyst compositions of Example 2 and Example 5 are presented in the following Table 1 and illustrated in the Figure.

TABLE 1

<u>2.6%Co/Beta[34]</u>		<u>3.9%Co/Beta[118]</u>	
Hours of Aging Conversion 25 @ 775°C (°C)	50% Conversion Temperature (°C)	Hours of Aging @ 775°C	50% Temperature
0	386	0	403
1172	440	729	407
1766	445	2943	425
30 2719	445	3706	424
3119	461	4465	424
3834	464	5367	428
4482	465	6321	429
5299	476	7591	429
35 6062	477	8647	427
6821	476	9477	433
7723	484		
8677	477		
9947	476		
40 11000	478		
11833	479		

-22-

Comparative Example 6 (4.02 wt.% Co/Beta [35.4] + 15% SiO₂)

The procedure of Example 5 was conducted using the Beta zeolite prepared in Example 3. The silica extrudates made were aged at 775°C and the T₀ was determined to be 484°C
5 at 3,165 hours.

While preferred and exemplary embodiments of the present invention have been described, the true scope of the invention is to be determined from the following claims.

-23-

What is claimed is:

1. A method comprising the step of catalytically reducing nitrous oxide with a catalyst comprising a zeolite which has been at least partially ion exchanged with at least one cation derived from at least one compound selected from the group consisting of hydrogen, ammonium containing compound, metals and metal compounds wherein the metal is selected from the group of metals below sodium on the Periodic Table of Elements, and where the zeolite has a molar ratio of silica to alumina of at least about 55.
2. The method as recited in claim 1 wherein the metal is selected from the group consisting of metals having the atomic number from Group 1a, 2a, 3a, 1b, 2b and transition metals having atomic numbers from 21 to 28, 39 to 46 and 72 to 78.
3. The method as recited in claim 2 wherein the metal is selected from the group consisting of cobalt, copper, rhodium, iridium, ruthenium and palladium.
4. The method as recited in claim 3 wherein the metal is cobalt.
5. The method as recited in claim 1 wherein the zeolite has been exchange with from 0.01 to about 15 weights percent of the metal based upon the total weight of the catalyst.
6. The method as recited in claim 1 wherein the nitrous oxide is reduced at temperatures of from about 200°C to about 800°C and pressures from about 0.1 to about 300 atmospheres.
7. The method as recited in claim 1 wherein the nitrous oxide is in a gas stream and the catalyst is in a reactor with the gas stream having a volume hourly space velocity of from 1,000 to 300,000 hours⁻¹.
8. The method as recited in claim 1 wherein the zeolite is selected from the group consisting of Beta, ZSM-5, Y, mordenite, and chabazite.
9. The method as recited in claim 8 wherein the zeolite is selected from the group consisting of Beta and

-24-

ZSM-5.

10. The method as recited in claim 9 wherein the zeolite is Beta.

11. The method as recited in claim 1 wherein the a
5 molar ratio of silica to alumina is from about 75 to about 200.

12. The method as recited in claim 1 wherein the a molar ratio of silica to alumina is from about 80 to about 175.

10 13. The method as recited in claim 1 wherein the a molar ratio of silica to alumina is from about 80 to about 120.

14. A method comprising the step of catalytically reducing nitrous oxide with a catalyst comprising a Beta
15 zeolite which has been at least partially ion exchanged with cobalt and where the zeolite has a molar ratio of silica to alumina of from about 75 to about 175.

15. The method as recited in claim 14 wherein the a molar ratio of silica to alumina is from about 100 to about
20 150.

16. A method of removing nitrous oxide from a gaseous stream comprising the steps:

controlling the molar ratio of silica to alumina of a catalyst comprising a zeolite, which has been at least
25 partially ion exchanged with at least one cation derived from at least one compound selected from the group consisting of metals and metal compounds wherein the metal is selected from the group of metals below sodium on the Periodic Table of Elements, ammonium and hydrogen, to
30 increase catalyst stability, and

contacting the gaseous stream with the catalyst under conditions sufficient to reduce at least part of the nitrous oxide to nitrogen and oxygen.

17. The method as recited in claim 16 wherein the
35 molar ratio of silica to alumina is increased to result in a T_{90} for nitrous oxide of less than about 450°C upon aging the catalyst in air at 775°C for 4,000 hours.

-25-

18. The method as recited in claim 17 wherein the molar ratio of silica to alumina is increased to result in a T_{50} for nitrous oxide of less than about 430°C upon aging the catalyst in air at 775°C for 4,000 hours.

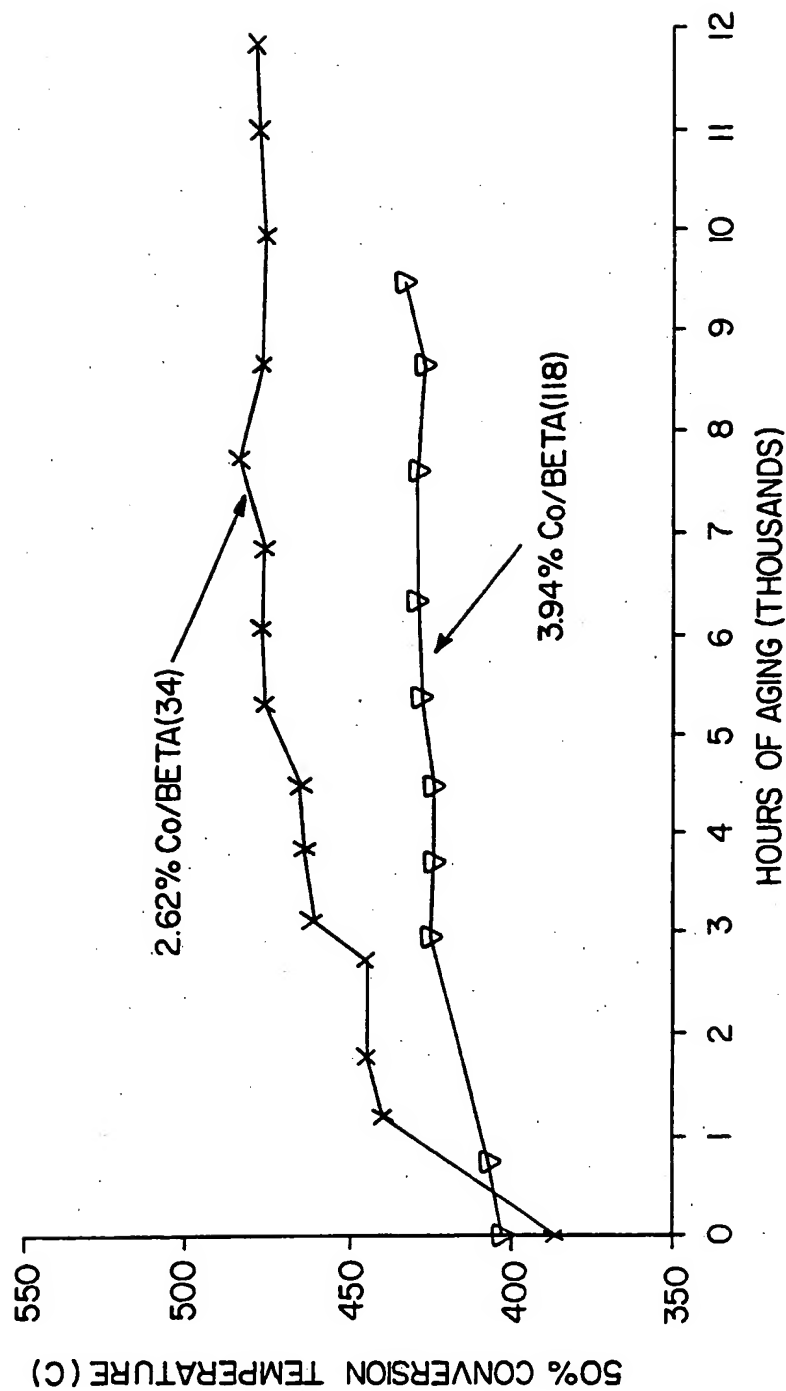
5 19. The method as recited in claim 16 wherein the step of increasing the silica to alumina ratio further comprises chemically treating the zeolite.

20. The method as recited in claim 19 where the step of increasing the silica to alumina ratio further comprises
10 reacting the zeolite with an acid.

21. The method as recited in claim 16 wherein the zeolite is Beta zeolite having an initial ratio of less than 55 and the step of increasing the silica to alumina ratio further comprises reacting the catalyst to increase
15 the ratio to greater than 65.

22. An improved method for catalytically reducing nitrous oxide in waste streams from processes selected from the group consisting of: adipic acid manufacture, nitric acid manufacture, the manufacture of hydroxyl amine
20 derivatives, the manufacture of caprolactam, processes for low temperature combustion of nitrogen containing materials and emissions from laughing gas anesthetics wherein the improvement comprises the step of catalytically reducing the nitrous oxide in said emissions with a catalyst
25 comprising a zeolite which has been at least partially ion exchanged with at least one cation derived from at least one compound selected from the group consisting of hydrogen, ammonium containing compound, metals and metal compounds wherein the metal is selected from the group of
30 metals below sodium on the Periodic Table of Elements, and where the zeolite has a molar ratio of silica to alumina of at least about 55.

1/1



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/03846

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 B01D53/36 B01J29/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMISTRY EXPRESS, vol.7, no.1, 1992 pages 77 - 80 TABATA ET AL. 'Catalytic performance of Cu and Co ion-exchanged zeolites for decomposition of NO and N2O' see page 80; figures 1-3; table 1 ---	1-4,8,9, 11-15
Y	US,A,5 171 553 (LI ET AL.) 15 December 1992 cited in the application see the whole document ---	1-22
Y	US,A,4 867 954 (STANIULIS ET AL.) 19 September 1989 see column 3, line 21 - column 4, line 56; claims 1-30 --- -/--	1-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 078 981 (KAGAWA ET AL.) 7 January 1992 see the whole document ---	1-3,5,6, 8,9, 11-18
A	EP,A,0 286 967 (BAYER AG) 19 October 1988 see claims 1-10; examples 1-7 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/03846

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